

Collective Nature of the Boson Peak and Universal Transboson Dynamics of Glasses

A. I. Chumakov,^{1,*} I. Sergueev,^{2,1} U. van Bürck,² W. Schirmacher,² T. Asthalter,³ R. Ruffer,¹ O. Leupold,¹ and W. Petry²

¹European Synchrotron Radiation Facility (ESRF), P.O. Box 220, F-38043 Grenoble, France

²Physik-Department E13, Technische Universität München, D-85748 Garching, Germany

³Physikalische Chemie II, Universität Stuttgart, D-70569 Stuttgart, Germany

(Received 12 December 2003; published 18 June 2004)

Using probe molecules with resonant nuclei and nuclear inelastic scattering, we are able to measure the density of states exclusively for collective motions with a correlation length of more than ~ 20 Å. Such spectra exhibit an excess of low-energy modes (boson peak). This peak behaves in the same way as that observed by conventional methods. This shows that a significant part of the modes constituting the boson peak is of collective character. At energies above the boson peak, the reduced density of states of the collective motions universally exhibits an exponential decrease.

DOI: 10.1103/PhysRevLett.92.245508

PACS numbers: 63.50.+x, 61.43.Fs, 64.70.Pf, 76.80.+y

Vibrational dynamics of glasses is a subject of controversial discussions. A focusing point of numerous studies is the “boson peak,” i.e., an excess of the low-energy density of states (DOS) in glasses relative to the Debye model. The boson peak is a distinct feature of most glasses and even disordered crystalline solids [1]. This makes it a touch stone for models of glass dynamics.

The basic question is: Does the boson peak originate from collective [2–4] or from local or “quasilocal” [5,6] motions? In many investigations, the boson peak is attributed to some local molecular-specific motion as intramolecular vibration [7], rotation of structural units [8], or conformational motion [9]. On the other hand, there is ample experimental evidence from scattering data [10–12] for a collective character of the modes composing the boson peak. This inconsistency can be clarified if one measures the DOS of collective and local motions separately. Here we report on model-independent measurements of the DOS exclusively for collective motions. The results evidence the predominantly collective character of the modes composing the boson peak. At the energies above the boson peak, the reduced DOS of the collective motions reveals a feature which is universal for all studied glasses: With astonishing accuracy it follows precisely an exponential dependence on energy.

In order to distinguish the collective motions from the local ones, we studied the glass dynamics using probe molecules. When a probe is embedded in a glass matrix, it obviously must follow the collective motions of the glass with a correlation length larger than the probe size. On the other hand, the vibrational spectrum of the probe is insensitive to local eigenmodes of the host, as long as the probe is not chemically bound. This insensitivity is confirmed by our experimental data. In order to monitor the motions of the probes, we used the isotope-selective technique of nuclear inelastic scattering (i.e., resonance inelastic scattering of x rays via low-energy nuclear transitions) [13–15] and probe molecules with a resonant nucleus in the center of mass. With this approach, one monitors exclusively the motions of the central resonant

nucleus. Furthermore, in this way one selects pure translational motions of the probes: Rotation is disregarded because the spectator nucleus is in the center of mass; the few intramolecular modes, as will be shown below, are separated in energy. Therefore, the selected pure translational motions of the probe give a “density of states of collective motions” (CDOS) of the glass matrix.

The CDOS in toluene, ethylbenzene, dibutylphthalate, and glycerol glasses was measured at the Nuclear Resonance beamline ID18 [16] of the European Synchrotron Radiation Facility with a 0.5 meV-bandpass inelastic spectrometer [17]. In terms of fragility m , the studied glasses cover a substantial part of the Angell diagram [18] as they represent very fragile (toluene, $m = 105$), fragile (dibutylphthalate, $m = 85$), and intermediate (glycerol, $m = 53$) glass formers [19–21]. The probes were neutral ferrocene molecules with the central resonant ^{57}Fe nucleus for the three first glasses and $^{57}\text{Fe}^{2+}$ ions for glycerol. The size of the ferrocene probe (7.3 Å) is close to those of the host molecules (7.0, 7.3, and 9.5 Å for toluene, ethylbenzene, and dibutylphthalate, respectively). To follow the collective motions of the glass, the probe should experience correlated forces at least from the nearest molecules. Thus, it is sensitive to the collective modes with a correlation length of more than ~ 20 Å. The concentrations of the probes for the above-mentioned glasses were 2.5, 2, 5, and 1% (mol). The probes did not cause noticeable changes in the glass properties. For instance, no changes in the static structure factor and in the calorimetric glass transition temperatures were revealed. Furthermore, lowering the probe concentration had no influence on the experimental results.

Figure 1(a) shows the DOS $g(E)$ of probe motions in toluene. Above 17 meV, it exhibits three narrow peaks. These are the only eigenmodes of the ferrocene probe which involve displacements of the central iron atom [23]. The vibrational states below 17 meV describe displacements of the rigid probe driven by the collective motions in toluene. For an *isolated* probe, the number of these states (the DOS integral in the 0–17 meV range)

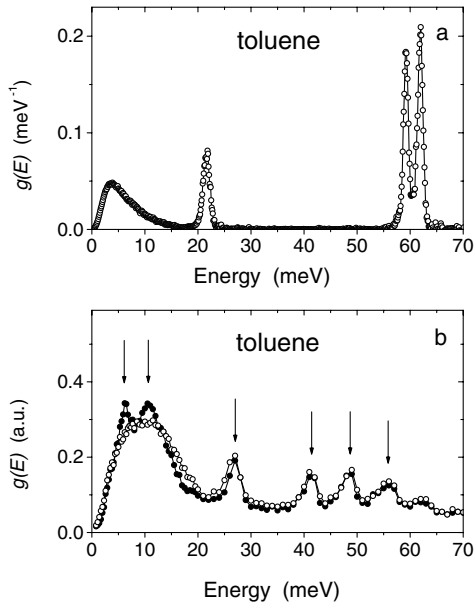


FIG. 1. Density of states (a) measured in toluene glass at 22 K using nuclear inelastic scattering from ferrocene probes in comparison to (b) neutron data for toluene glass (\circ) and crystal (\bullet) [22]. Solid lines are to guide the eyes. Arrows indicate the local vibrational modes of toluene.

should be equal to the mass ratio of ^{57}Fe to ferrocene [24]. The measured value of 0.33(2) coincides with the mass ratio (0.305) almost exactly. This proves that the probes are not locally bonded to the glass molecules (otherwise the effective mass of the probe would be significantly larger). Thus, one can expect that the probes will not “see” the eigenmodes of the neighbor glass molecules.

The insensitivity of the probes to local vibrations in the glass is testified by comparison to the total DOS available from neutron data [Fig. 1(b)]. In toluene, the probes do not see the rotations (7 and 11 meV) and librations (27 meV) of the methyl group [22] as well as other local modes at higher energies. The same holds for the ethylbenzene and dibutylphthalate data. By contrast, in glycerol the Fe^{2+} ions are bound to glass molecules and do show obvious peaks of local vibrational modes. These peaks, however, are located above 8 meV, still allowing for the investigation of collective motions at lower energies.

The reduced CDOS $g(E)/E^2$ clearly exhibits a boson peak for all studied glasses (Fig. 2). The positions E_B of the peak are consistent with the boson peak energies $E_{B\text{tot}}$ in the total DOS from neutron and light scattering data (Table I). The temperature evolution of the boson peak (Fig. 2) shows the same features as observed with conventional methods: It is temperature independent at low temperatures, becomes less pronounced at higher temperatures, and disappears when approaching the glass-liquid transition. This clear manifestation of the boson peak in the CDOS shows that the significant part of the modes constituting the boson peak must be the delocal-

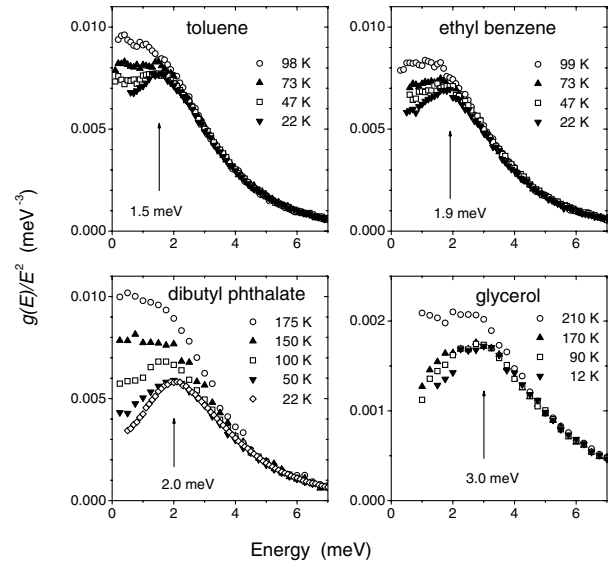


FIG. 2. Reduced DOS of collective motions in toluene, ethylbenzene, dibutylphthalate, and glycerol glasses. Arrows indicate the energy of the boson peak estimated from the data at lowest temperature.

ized collective motions with the correlation length of more than $\sim 20 \text{ \AA}$.

Beyond the boson peak, the reduced density of states of collective motions reveals for all studied glasses a *temperature-independent*, precisely *exponential* behavior:

$$g(E)/E^2 \propto \exp(-E/E_0), \quad (1)$$

which, to our best knowledge, was not reported earlier. Quite intriguing, the characteristic “decay” energies E_0 correlate with the energies of the boson peak E_B (Table I). Note that, differentiating Eq. (1), one finds that E_0 is related to the position E_{max} of the CDOS maximum as $E_0 = 0.5E_{\text{max}}$.

Figure 3(a) shows that Eq. (1) describes the CDOS perfectly at high energy, still quite well near the maximum, and starts to fail approaching the energy of the boson peak. In a log scale, $g(E)/E^2$ follows a straight line over *three decades* of the reduced CDOS and starts to deviate from Eq. (1) only when obscured by

TABLE I. The energy positions of the boson peak in the density of states of collective motions (E_B), in the total density of states from neutron and light scattering data ($E_{B\text{tot}}$), and the “decay” energy E_0 obtained from the fit of the CDOS with Eq. (1).

Glass	E_B (meV)	$E_{B\text{tot}}$ (meV)	E_0 (meV)
Toluene	1.5	1.6 [25]	1.9
Ethylbenzene	1.9	2.0 [26]	1.9
Dibutylphthalate	2.0	2.2 [27]	2.0
Glycerol	3.0	3.8 [28]	2.8

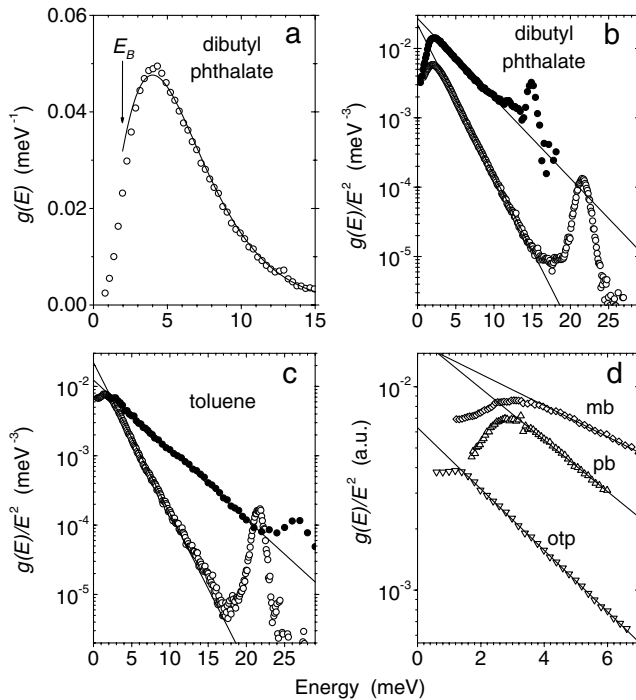


FIG. 3. (a) DOS of collective motions in dibutylphthalate at 22 K. Reduced DOS of collective motions in (b) dibutylphthalate and (c) toluene at 22 K (\circ) in comparison to reduced total DOS (\bullet) from neutron data [22,27]. The neutron data are scaled to match our data at lowest energy. (d) Reduced total DOS from neutron data for orthoterphenyl (otp, ∇) [29], polybutadiene (pb, \triangle) [30], and myoglobin (mb, \diamond) [31]. Solid lines show the fit according to Eq. (1). The arrow indicates the energy of the boson peak E_B .

the eigenmode of ferrocene at 22 meV [Figs. 3(b) and 3(c)]. This tremendously large “dynamical range” allows for a clear identification of the CDOS behavior with Eq. (1) and hardly permits any alternative functional form. In particular, this excludes a description in terms of a power law [5] or a log-normal [6] behavior, obtained for *local* and *quasilocal* vibrations, respectively.

Because the exponential behavior is so pronounced in the CDOS, one could also expect to trace it in the total DOS. We indeed found it in the neutron data for all glasses studied here [22,26,27,32] as well as for other molecular glasses (salol, orthoterphenyl), polymers (polybutadiene, polyisobutylene), and proteins (myoglobin) [33,29,30,34,31]. The most evident examples are shown in Figs. 3(b)–3(d).

In comparison to the total DOS, the CDOS exhibits slightly lower energy of the boson peak (Table I) and a considerably steeper exponential slope [Figs. 3(b) and 3(c)]. Around the boson peak, it shows an approximately 2 times smaller number of states than the total DOS [Fig. 3(b)].

These differences allow for two alternative interpretations. A straightforward approach is to attribute the difference between the total DOS and CDOS to the local

modes. Then one could conclude that (i) the boson peak is composed by both collective and local motions, (ii) the collective part has a slightly lower energy relative to the local one, and (iii) the collective states have less spectral weight in the high-energy region of the DOS. Similar conclusions were obtained recently from a neutron scattering experiment, where the total DOS was decomposed into an in-phase and a random-phase component using the model of umklapp scattering [11,12].

An alternative interpretation—which we favor—is based on the fact that, similar to the CDOS, the total DOS exhibits the exponential behavior as well. In toluene, for instance, the total DOS follows Eq. (1) in the energy range up to 22 meV and over two decades of $g(E)/E^2$ [Fig. 3(c)]. This gives an indication that the boson peak could be composed by pure collective modes, and the difference between the total DOS and CDOS comes not from local modes but from different correlation lengths accessible with various techniques. The CDOS is measured by the ferrocene probes sensitive to collective motions with a correlation length of more than ~ 20 Å. The total DOS as derived from neutron scattering is mainly probed by the hydrogen atoms constituting the bulk material. Therefore, it can include collective motions with much smaller correlation length.

Such a probe size effect can be analyzed within a model dealing with a finite generalized mean-free path of vibrational modes (e.g., [2]). Introducing a spatial cut-off of the probe sensitivity given by the probe radius R_0 , one arrives at Eq. (1) with $E_0 = \hbar c_0^2 / (c'' R_0)$, where c_0 is the sound velocity and c'' is the imaginary part of a generalized complex sound velocity introduced by disorder, which is almost frequency independent in the trans-boson regime [35]. E_0 is inversely proportional to the effective probe size, which supports the above interpretation.

We also checked the validity of Eq. (1) by numerical calculations within a collective model with fluctuating elastic constants, described in self-consistent Born approximation (SCBA) [36,37], a modification of the coherent-potential approximation (CPA) suitable for non-crystalline solids. The CPA successfully reproduces the boson peak in models of randomly fluctuating elastic constants and identifies it with the collective motions [2,3]. The SCBA contains only a single disorder parameter, namely, the variance γ of the elasticity fluctuations. Figure 4 shows the reduced DOS calculated for various values of γ . In the energy region between the boson peak and the Debye energy E_D , the calculations are consistent with Eq. (1). At higher energy, Eq. (1) cannot be verified with the SCBA (which is not applicable above E_D), but agrees with the results of molecular dynamics simulations [38], which do not show significant discontinuity at E_D (Fig. 4).

In summary, we measured the density of states exclusively for collective motions with a correlation length of

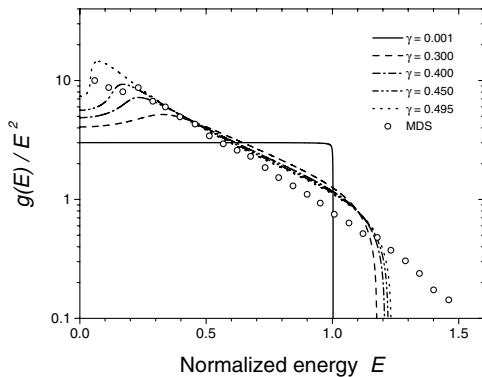


FIG. 4. Reduced density of states calculated for several variances γ of the elasticity fluctuations in self-consistent Born approximation (lines) in comparison to molecular dynamics simulations (MDS) data [38] for a “Lennard-Jones glass” (\circ). The energy of excitations is normalized to the Debye energy E_D .

more than $\sim 20 \text{ \AA}$ for several molecular glasses. This CDOS reveals a boson peak and exhibits its typical temperature evolution. This shows that a significant part of the modes constituting the boson peak is of collective character. Beyond the boson peak, the reduced DOS of collective motions reveals very precisely an exponential dependence on energy. A similar exponential behavior is also found for the total DOS of the same (and other) glasses in neutron scattering data but with a less steep slope. This difference between the total DOS and the CDOS allows for two different interpretations: It can be attributed to additional local modes in the total DOS at higher energies or, alternatively, can be explained within a pure collective model assuming a lower sensitivity of the relatively large molecular probes to collective vibrations with short wavelengths. One can expect to settle this question by studying the collective DOS with probes of variable size.

We thank G. J. Cuello, A. Mermet, and O. Yamamuro for providing their neutron data, B. Frick, A. Tölle, R. Verbeni, and J. Wiedersich for technical advice, H. Müller for DSC measurements, and E. Duval, A. Ivanov, E. Kats, V. Kohn, G. Ruocco, and A. Sokolov for discussions. Part of this work has been supported by the German BMBF under Contract No. 05 KSIWOC/2.

*Author to whom correspondence should be addressed.
Electronic address: chumakov@esrf.fr
Also at Russian Research Center “Kurchatov Institute,”
123182 Moscow, Russia.

- [1] *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).
[2] W. Schirmacher, G. Diezemann, and C. Ganter, *Phys. Rev. Lett.* **81**, 136 (1998).

- [3] S. N. Taraskin, Y. L. Loh, G. Natarajan, and S. R. Elliott, *Phys. Rev. Lett.* **86**, 1255 (2001).
[4] T. S. Grigera, V. Martin-Mayor, G. Parisi, and P. Verrocchio, *Nature (London)* **422**, 289 (2003).
[5] V. L. Gurevich, D. A. Parshin, and H. R. Schober, *JETP Lett.* **76**, 553 (2002); *Phys. Rev. B* **67**, 094203 (2003).
[6] V. K. Malinovsky, V. N. Novikov, and A. P. Sokolov, *Phys. Lett. A* **153**, 63 (1991).
[7] O. Yamamuro *et al.*, *J. Chem. Phys.* **106**, 2997 (1997).
[8] U. Buchenau, N. Nücker, and A. J. Dianoux, *Phys. Rev. Lett.* **53**, 2316 (1984).
[9] J. Colmenero, A. Arbe, and A. Alegria, *Phys. Rev. Lett.* **71**, 2603 (1993).
[10] C. Masciovecchio, A. Mermet, G. Ruocco, and F. Sette, *Phys. Rev. Lett.* **85**, 1266 (2000).
[11] U. Buchenau, A. Wischnewski, D. Richter, and B. Frick, *Phys. Rev. Lett.* **77**, 4035 (1996).
[12] A. P. Sokolov, *J. Phys. Condens. Matter* **11**, A213 (1999).
[13] M. Seto, Y. Yoda, S. Kikuta, X. W. Zhang, and M. Ando, *Phys. Rev. Lett.* **74**, 3828 (1995).
[14] W. Sturhahn *et al.*, *Phys. Rev. Lett.* **74**, 3832 (1995).
[15] A. I. Chumakov *et al.*, *Europhys. Lett.* **30**, 427 (1995).
[16] R. Ruffer and A. I. Chumakov, *Hyperfine Interact.* **97–98**, 589 (1996).
[17] A. I. Chumakov *et al.*, *Appl. Phys. Lett.* **77**, 31 (2000).
[18] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, *J. Appl. Phys.* **88**, 3113 (2000).
[19] A. Döb, G. Hinze, B. Schiener, J. Hemberger, and R. Böhmer, *J. Chem. Phys.* **107**, 1740 (1997).
[20] A. Mermet, E. Duval, A. Polian, and M. Krisch, *Phys. Rev. E* **66**, 31510 (2002).
[21] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).
[22] I. Tsukushi *et al.*, *J. Phys. Chem. Solids* **60**, 1541 (1999).
[23] E. Kemner, I. M. de Schepper, G. J. Kearley, and U. A. Jayasooriya, *J. Chem. Phys.* **112**, 10926 (2000).
[24] A. I. Chumakov, R. Ruffer, O. Leupold, and I. Sergueev, *Struct. Chem.* **14**, 109 (2003).
[25] J. Wiedersich, N. V. Surovtsev, and E. Rössler, *J. Chem. Phys.* **113**, 1143 (2000).
[26] B. Frick, J. Williams, S. Treviño, and R. Erwin, *Physica (Amsterdam)* **213B&214B**, 506 (1995).
[27] E. Duval *et al.*, *J. Non-Cryst. Solids* **307–310**, 103 (2002).
[28] J. Wuttke *et al.*, *Phys. Rev. Lett.* **72**, 3052 (1994).
[29] A. Tölle *et al.*, *Eur. Phys. J. B* **16**, 73 (2000).
[30] R. Zorn *et al.*, *Phys. Rev. E* **52**, 781 (1995).
[31] W. Doster, S. Cusack, and W. Petry, *Phys. Rev. Lett.* **65**, 1080 (1990).
[32] G. J. Cuello *et al.*, *Phys. Rev. B* **57**, 8254 (1998).
[33] R. Zorn, D. Richter, L. Hartmann, F. Kremer, and B. Frick, *J. Phys. IV (France)* **10**, Pr7-83 (2000).
[34] K. Inoue *et al.*, *J. Chem. Phys.* **95**, 5332 (1991).
[35] W. Schirmacher (unpublished).
[36] S. John, H. Sompolinsky, and M. J. Stephen, *Phys. Rev. B* **27**, 5592 (1983).
[37] W. Schirmacher, M. Pöhlmann, and E. Maurer, *Phys. Status Solidi (b)* **230**, 31 (2002).
[38] A. Rahman, M. J. Mandell, and J. P. McTague, *J. Chem. Phys.* **64**, 1564 (1976).